LA-UR-04- 1405

Title: MODELING OF AN ATMOSPHERIC-PRESSURE HE/CF4/
O2 PLASMA USED FOR SURFACE DECONTAMINATION
(Paper for proceedings)

Author(s): H.L. Teslow, L.A. Rosocha, and Y. Kim
Plasma Physics Group, P-24

Submitted to: 4th International Symposium on Non-Thermal Plasma
Technology for Pollution Control and Sustainable Energy
Development (ISNTP-4)

Panama City, FL
May 10-14, 2004

Los Alamos
NATIONAL LABORATORY

MODELING OF AN ATMOSPHERIC-PRESSURE HE/CF$_4$/O$_2$ PLASMA USED FOR SURFACE DECONTAMINATION

Hilary L. Teslow*[1,2], Louis A. Rosocha[1], and Yongho Kim[1]

[1]Los Alamos National Laboratory, Los Alamos, NM 87544

[2]University of Michigan, Ann Arbor, MI 48105

Abstract Atmospheric-pressure plasmas have been shown to be useful in many different applications, including surface decontamination. We will describe a useful plasma source, a non-thermal Atmospheric-Pressure Plasma Jet (APPJ), for such applications. In recent APPJ experiments, a plasma consisting of helium mixed with small percentages of carbon tetrafluoride and molecular oxygen was used to etch tantalum foils as well as plutonium on the surface of a sample metal coupon. Understanding the plasma, chemical, and surface kinetics of this plasma is crucial to the widespread application of this procedure to various contaminants, such as chemical and biological warfare agents (CBW). A complete, detailed model of the plasma, post-plasma gas chemistry, and surface chemistry is needed to determine the reactive species and exact surface reactions occurring in each of the experiments. Using commercial software (KINEMA and ELENDIF), we have created a post-plasma gas chemistry model which utilizes over 180 chemical reactions and initial conditions determined by gaseous electronics modeling. Multiple reaction reduction techniques were used to ascertain the most important reactions and relevant species. This model indicates that although fluorine may be a reactive species, other oxyfluorides such as OF, F$_2$O, and FCOO most likely contribute significantly to the etching process. Comparison with experimental data suggests that fluorine is not the sole etchant.

1. Introduction

In recent studies, the Atmospheric-Pressure Plasma Jet (APPJ) and other non-thermal atmospheric-pressure plasma sources have proven to be successful means of etching certain contaminants (1, 2, 3, 4). Optimization of these devices to decontaminate various hazardous materials has led to the need for a detailed model of the plasma processes involved in etching. Before we can apply these techniques to other materials, namely chemical and biological warfare (CBW) agents, we must first determine the reactive species and products that are created by the reactions of the gases in the plasma and the reactions of the plasma-process gases with the surfaces in question. The model must include components describing the plasma, chemical, and surface kinetics within the system. The plasma kinetics component of the model should incorporate relevant cross sections of helium, carbon tetrafluoride, and molecular oxygen at atmospheric pressure to establish the initial concentrations of each molecular species exiting the plasma stage. Air does not appear to be a significant enough fraction of the gas inside the APPJ to force the inclusion of nitrogen and other atmospheric gases in the model. The chemical component of the model should include significant reactions between the primary gases and their reaction byproducts in the post-plasma region. The third component should model the surface kinetics where the post-plasma compounds and the material being etched react.

We have constructed a chemical kinetics model in KINEMA, a general plasma chemistry code developed by W. L Morgan and Kinema Research. It comprises over one hundred and eighty chemical reactions and uses as input parameters the initial concentrations of the primary gases – carbon tetrafluoride and molecular oxygen – and species directly derived from them in the plasma. These initial concentrations were determined by ELENDIF, the companion program to KINEMA, which solves the time-dependent Boltzmann equation for a given mixture of partially ionized gases.

2. Procedure

2.1 Experimental Background

In the APPJ experiments, helium gas is mixed with small amounts of carbon tetrafluoride and molecular oxygen (e.g., 2% O$_2$ and 4% CF$_4$). Helium serves as an inert carrier gas for the reactions of the more volatile gases; its flow rate is typically around 25 slpm. The gas mixture streams through an annular channel that surrounds a cylindrical RF electrode. (See Figure 1) The applied power (usually around 500 W at 13.56 MHz) supplies the energy to create a plasma and dissociate CF$_4$ and O$_2$ into molecular fragments, ions, and electrons. A

1

cylindrical collimator may be inserted between the annular region and the nozzle. By increasing the standoff distance between the plasma generation region and the surface being etched, a collimator promotes reactions between gaseous products by minimizing their diffusion. The collimators used in our experiments were between 50 and 210 mm in length; the original standoff distance with no collimator is 3 mm.
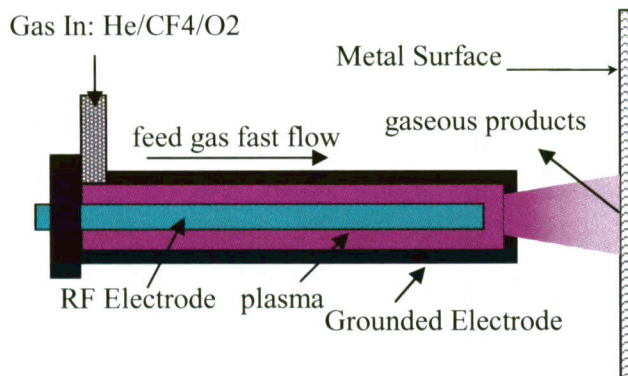
Gas In: He/CF4/O2

Figure 1

The gas leaves the nozzle at a temperature of about 373 or 573 K, depending on the amount of cooling used around the jet. The two jets used in our experiments both have water cooling systems around the outer electrode. The "cooled" jet has additional cooling around the inner RF electrode. The linear velocity generated by a flow rate of 25 slpm at these temperatures is between 20 and 40 m/s. The tantalum foils used as plutonium surrogates measure 0.025 mm thick, and are spot-welded to metal coupons and placed on a heated platform, directly beneath the nozzle. The platform temperature can be increased to approximately 573 K; during operation this temperature further increases by 100 – 200 K due to the elevated temperature of the gas leaving the jet.

2.2   Kinetics of Reactions   Helium was chosen as the primary gas because of its low breakdown voltage, large stable operating window, and high thermal conductivity, which helps with cooling. The combination of carbon tetrafluoride and molecular oxygen in the gas mixture produces higher etch rates than either gas by itself. Optimum levels of each were established through experiments. The plasma dissociates CF_4 into various ions and neutral fragments, including atomic fluorine, while some percentage of O_2 is also converted to ions and neutrals, as well as metastable states. Before exiting the jet through the nozzle, the molecular fragments and plasma products react with one another, forming additional species. Outside of the nozzle, the neutral particles continue to react with each other in the post-plasma region; ions and electrons recombine within a few hundred micrometers at atmospheric pressure (6). The interactions of the primary species, O, F, and CF_x radicals produce many different reactants. There are over two hundred reactions (some of which have incomplete data

or unknown products and thus are not included in the ~180 used in the model) that can occur between oxygen, carbon, fluorine, and the numerous combinations of these elements, leading to very complicated post-plasma chemistry. Some of these species react with the surfaces, etching the metal and creating volatile gases. The purpose of our model is to determine which of these molecules and elements are responsible for the etching.

2.3   Developing the Model   The first step in creating our model was to do an extensive literature search to find current rate constants for all relevant reactions involving carbon tetrafluoride, molecular oxygen, and the products formed in the plasma. Ions and electrons are neglected in the post-plasma model because, as mentioned previously, they recombine almost immediately after leaving the jet. The NIST Chemical Kinetics Database (5) is the source for the majority of the reactions and rate coefficients used in the chemical model. Data for certain rate coefficients at the elevated temperatures of our experiment is limited, but the list we have compiled is comprehensive if not entirely complete. All available, accessible data was incorporated into this model.

Once the data was accumulated, the reactions and rate coefficients were put into files used by the KINEMA code. Running the program in KINEMA provided us with graphs of the populations of each species that are found in the post-plasma region as a function of gas transit time from the APPJ exit.

2.4   Reaction Reduction   From the over one hundred eighty reactions in the original KINEMA model, we then reduced the reaction set to the most crucial reactions by ascertaining whether or not a particular reaction affects the populations of the key species. This was done to extract the reactions and species which are most important for our experiments. KINEMA allows the user to adjust the plasma input parameters to match each run to specific plasma-processing effluents.

The first reaction reduction technique used involved examining the rate constants and reactants of each reaction. The reactions were then categorized in terms of how much overall effect that particular reaction had on the reactants and products involved, relative to other reactions containing those species. That is, we arranged the change in concentration, Δ_{ij}, in ascending order, where Δ is described by the following equation:

$$\Delta_{i,j} = k_{i,j} * [R_i] * [R_j],$$

for the reaction

$$R_i + R_j \rightarrow P_l + P_m$$
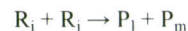
where k is the temperature dependent rate coefficient and $[R_i]$ and $[R_j]$ are the estimated initial concentrations of the first and second reactant, respectively.

The second iteration of the reaction reduction process was simply eliminating those chemical species that were not

produced in significant amounts (the population was less than 10^5 cm^{-3}). In the same manner, reactions containing reactants whose populations were indicated to be less than 10^{11} cm^{-3} were scrutinized individually to ensure they had no effect on the populations of any significant species. This group of molecules included F_2O_2, CF_3OF, CF_3COF, FCOOOOCF, and CF_3OOOCF_3. From these graphs, certain species were found to be largely irrelevant to the etching process since their concentrations were negligible (less than 10^{11} cm^{-3}; essential species have populations around 10^{15} cm^{-3}). The key species are those that have sufficient populations to either be etchants or contribute to etching by directly affecting the primary reactive species. They are F, F_2, O, O_3, OF, F_2O, CO, CO_2, COF_2, FCOO, $FCOO_2$, and CF_3O_2. The populations of these species as calculated by our model using typical experimental parameters are shown in Figure 2.
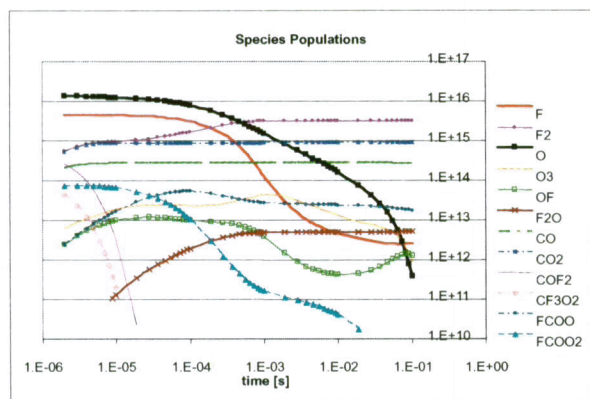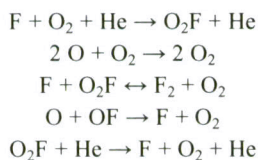

Figure 2

The final iteration consisted of studying each reaction individually and observing whether it affected any of the key species. This was done by comparing graphs of all relevant populations generated with each reaction eliminated from the model, and comparing them to those created with the original reaction set. The reduced reaction set of 34 reactions appears to produce the same results (populations) of the key species as the original, thus indicating that these are the most important equations. The most significant of these are the following:

$$F + O_2 + He \rightarrow O_2F + He$$
$$2\,O + O_2 \rightarrow 2\,O_2$$
$$F + O_2F \leftrightarrow F_2 + O_2$$
$$O + OF \rightarrow F + O_2$$
$$O_2F + He \rightarrow F + O_2 + He$$

These equations appear to have the most effect on the populations of key species under our experimental conditions. Other significant reactions involve CF_x and $FCOO_x$ radicals, as well as excited states of O and O_2. CO and CO_2 also have substantial concentrations, but it is unlikely that these

molecules are etchants. Thus it appears that the most important species are fluorine, atomic oxygen, and a variety of oxyfluorides, implying that some or all of these contribute to the etching process. The validity of our model can be tested by comparing the results it generates to experimental data.

3. Comparison with Experimental Data

3.1 Etch Rate The etch rate is determined by the number of reactive species that reach the metal surface. The etch rate depends on several different parameters. These include standoff distance, O_2 and CF_4 concentrations, jet temperature, substrate temperature, applied power, helium flow rate, and size of the tantalum foils. We compared the results of the model with data from experiments testing the standoff distance, jet temperature, and O_2 concentration.

3.2 Standoff Distance The variation of etch rate with standoff distance is of particular interest because it indicates the lifetime of the reactive species. The etch rate was measured using each collimator. As expected, the etch rate decreased as the standoff distance increased. The fact that etching occurred with a 210 mm collimator indicated that at least one of the reactive species must be fairly long-lived. The transit time, calculated using the various lengths of the collimators and the linear velocities for each temperature, is consistently in the millisecond range. Figure 3 shows the species that the model indicates have the highest concentrations over that time range, and thus are most likely to reach the metal surface and bring about etching. Note that fluorine, which had been presumed to be responsible for etching, is not the only species that lives long enough to be the etchant.
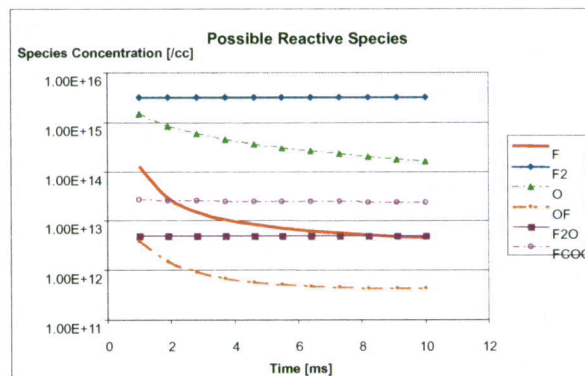

Figure 3

3.3 Jet Temperature We also considered species population dependence on jet temperature. Etch rates were measured for various standoff distances using the two APPJs described previously. The etch rate was consistently higher when using the jet with only outer electrode cooling. See

Figure 4. We ran the KINEMA code at temperatures characteristic of the two APPJs and examined the species populations. According to our simulations, F atoms and many oxyfluorides like OF, COF_2, CF_3O_2, and $FCOO_2$ live longer at higher temperatures, while O atoms have about the same lifetime. This indicates that fluorine and oxyfluorides are most likely responsible for the etching that occurs on the metal surfaces.
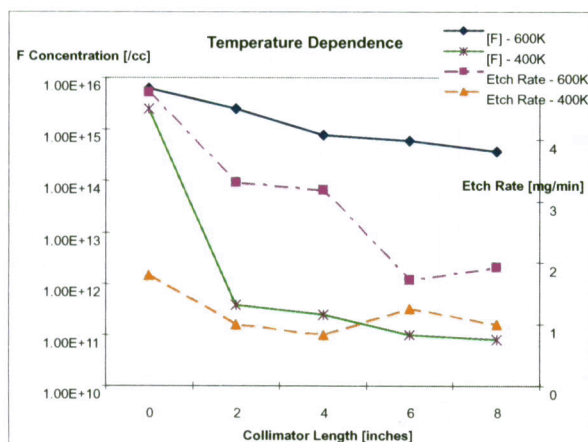

Figure 4

3.4 O_2 Dependence The amount of molecular oxygen in the gas stream also has a noteworthy affect on the etch rate. We measured the etch rate at a variety of different O_2 percentages from 0% to 4%, above which the plasma becomes unstable, while holding constant the gas flow rates and all other parameters. With no oxygen flowing, the He/CF_4 plasma yielded very low etch rates; at the optimum O_2 concentration ($\sim$ 2%) the etch rate was almost eight times higher. We ran the model with the initial concentrations of O_2 and its derivatives set to zero, expecting to see the fluorine radical disappear. However, atomic fluorine appeared to live longer with 0% than with 2% oxygen. In the relevant time range, both atomic and molecular fluorine maintained similar concentrations in the presence and the absence of O_2. The majority of other key species did drop to near zero. The abundance of fluorine predicted by the model combined with the low experimental etch rates indicate that fluorine may be partially responsible for etching, but cannot be the sole reactive species generated by the $He/CF_4/O_2$ plasma.

4. Conclusions The chemical kinetics model we have developed is the first step in determining the reactive species responsible for etching tantalum and plutonium in the APPJ experiments. The gas chemistry model of the post-plasma stage indicates that fluorine is not the only reactive species, and it is likely that some oxyfluorides contribute significantly to the etching of metal surfaces. This was determined based on the results of the reaction reduction performed to isolate the crucial reactions, and comparison with experimental data and other atmospheric-pressure models (7, 8). A detailed plasma kinetics model and a model of the region where post-plasma gases react with the metal surface are still necessary to completely understand the dynamics of the entire etching process. More experimental data, including spectroscopic measurements, is also needed for comparison, and will be performed in the near future.

References

(1) V. J. Tu, J.Y Jeong, A. Schutze, S.E. Babayan, G. Ding, G. S. Selwyn, and R. F. Hicks : "Tantalum etching with a nonthermal atmospheric-pressure plasma", Journal of Vacuum Science and Technology, Vol.18, No. 06, pp.2799-2805 (pub. 2000)

(2) G. S. Selwyn, H. W. Herrmann, J. Park, and I. Henins : "Materials Processing Using an Atmospheric-Pressure RF-Generated Plasma Source", Contributions to Plasma Physics, Vol.41, No.06, pp.610-691 (pub. 2001)

(3) J. Y. Jeong, S. E. Babayan, V. J. Tu, J. Park, I. Henins, R. F. Hicks, and G. S. Selwyn : "Etching materials with an atmospheric-pressure plasma jet", Plasma Sources Science and Technology, Vol.07, No.03, pp.282-285 (pub. 1998)

(4) P. Koulik, S. Begounov, and S. Goloviatinskii : "Atmospheric plasma sterilization and deodorization of dielectric surfaces", Plasma Chemistry and Plasma Processing, Vol.19, No.02, pp.311-326 (pub. 1999)

(5) "NIST Chemical Kinetics Database", dist. by Standard Reference Data Program, National Institute of Standards and Technology, Gaithersburg, MD (1998)

(6) Schutze A, Jeong J Y, Babayan S E, Park J, Selwyn G S, andHicks R F : "title", 1998 IEEE Trans. Plasma Sci., Vol.23, pp.1685-000 (pub. 1998).

(7) X. Yang, S. E. Babayan, and R. F. Hicks : "Measurement of the fluorine atom concentration in a carbon tetrafluoride and helium atmospheric-pressure plasma", Plasma Sources Science and Technology, Vol.12, No.03, pp.484-488 (pub. 2003)

(8) I. C. Plumb and K. R. Ryan : "A Model of the Chemical Processes Occurring in CF4/O2 Discharges Used in Plasma Etching", Plasma Chemistry and Plasma Processing, Vol.06, No.03, pp.205-230 (pub. 1986)